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The undersigned hereby certify that they have read and recommend to the Committee on Graduate Studies for acceptance, a dissertation on the "Solubility of Some Alberta Coals" submitted by Harold George Reiber, B. Sc. in partial fulfilment of the requirements for the degree of Master of Science.

Professor

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Thesis
1930
#11

S O L U B I L I T Y O F S O M E A L B E R T A C O A L S

- by -

HAROLD GEORGE REIBER, B. Sc.

Research Council of Alberta

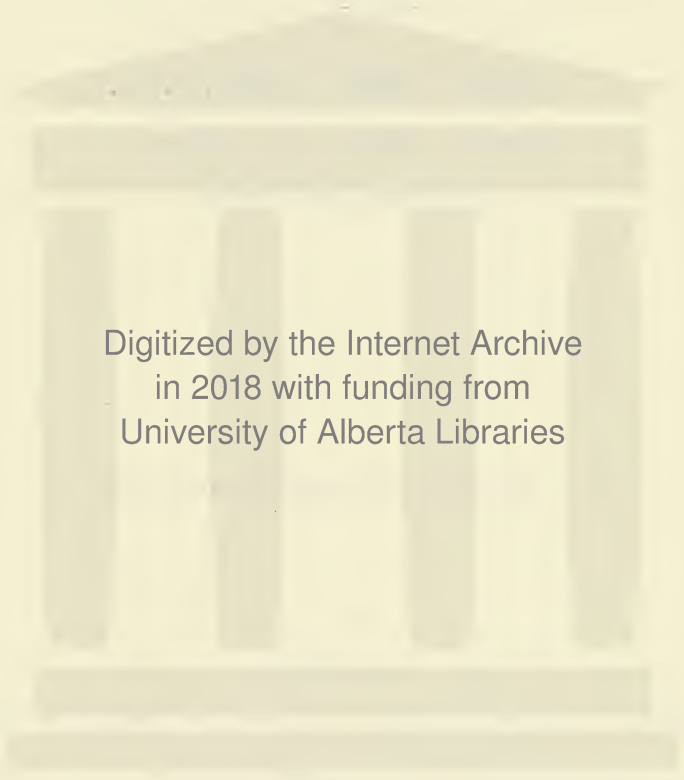
University of Alberta

A T H E S I S

Submitted to the University of Alberta in Partial Fulfilment
of the Requirements for the Degree of Master of Science.

Edmonton, Alberta.

April, 1930.



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A C K N O W L E D G M E N T S.

The investigation described in this thesis was carried out in the laboratories of the Research Council of Alberta.

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T H E S O L U B I L I T Y O F S O M E
A L B E R T A C O A L S .

CHAPTER I .

I N T R O D U C T I O N .

1. General.

The economic importance of coal to the industrial development of any country has been apparent for many years. This dependency on coal has been somewhat lessened by the use of alternative fuels, such as oil and gas, and by the development of hydroelectric power. Coal, in the majority of countries, remains the main source of energy on account of its wide occurrence and low cost. The Alberta coal fields are, unfortunately, far from any large market, but it is hoped, that, in the not too distant future, wider markets may be developed and Alberta's coal become more valuable.

Coal, being a product of nature of such significance in this age of power, has naturally been the subject of many chemical investigations. Tests have been employed for many years, which tell us the value of the coal as a source of heat and power, but it is only within the last twenty years that any very definite information as to its chemical constitution has been advanced. The wide divergence of the many types of coal probably indicates both qualitative and quantitative differences, and each type must be investigated.

The extraction of coal with organic solvents has been of particular value in this more comprehensive study, for it has been possible to separate some of the components and thus study their individual properties. The investigations along these lines are still in progress, and many different methods are being tried with varying success, and occasionally conflicting results. The results obtained, however, amply justify the continuation of such researches. There is also the probability that more complete knowledge of the constitution of coal will lead to its greater use as a raw material for chemical industries. The extraction of montan wax from the German brown lignites has been a profitable industry for some time. This wax is used extensively in the manufacture of boot polish, floor polish, special waxes, lacquers, electric insulation, etc. When bleached it becomes pale yellow in colour and can be used for light coloured floor polishes, and as a hardener for paraffin wax in the manufacture of candles.

2. Object of the Research.

No general survey had previously been made of Alberta coals as to their solubility in any solvent. While the yields of extract were not expected to be very high, it was thought possible that some freak coal might be found, which on extraction with one of the more common and inexpensive solvents would yield a substance similar to the bitumen or montan wax extracted from the German lignites. Interest had been aroused by the statement of a German authority that the development of any coal yielding 8% montan wax would be economically profitable. Again the so-called "fuel ratio" of coal has not been tied up with any one characteristic of the coal, and it was suggested that some relation might be found to exist between the yield of extract and this ratio. Furthermore, there are three distinct

types of coal in Alberta; bituminous, sub-bituminous, and lignite, with varying carbon and oxygen content. A comparison of the ultimate analyses of the coals and their extracts would show the relation between the carbon, hydrogen, and oxygen contents of a coal and its extract, and the effect of the transformation of a lignite to a bituminous coal, on the soluble portion of the coal.

The aim of the author in attempting this research was not particularly to determine any of the components of Alberta coals. Although much has been done in this field on other coals, and it is quite probable that our coals differ materially, the problem was too big. Neither was the problem of the coking constituents of coal investigated, although a great deal of the previous work on solubility was tied up with this property of some coals.

This preliminary survey would indicate the advisability of continuing the extraction of the many types of Alberta coals with either the solvents used, or any others which might be selected. If some use could be found for the extract or any of its components, the development of an industry which would use coal as its raw material would tremendously enhance the present value of the coal resources of this province.

CHAPTER II.

CONSTITUTION OF COAL.

1. Theories of formation.

It is generally accepted that coal is of vegetable origin and that any animal or mineral matter present had no significant effect in its formation. Undoubtedly one of the first stages in this important transformation is from the plant to peat, which is found in such widely distributed areas. This early stage is probably the result of oxidation of the vegetable matter by bacteria, with a limited supply of air. Hence we have an increase in the percentage of carbon, and a decrease in the percentage of oxygen, in the peat as compared to the plant. This action continues under varying conditions for some time, but it is likely that the pressure of superincumbent sediments, extending over long periods of time, is needed for the later transformations. The gases formed during the early conversion of vegetable matter to peat will probably escape; later, when the air is shut off, they may be imprisoned. Some coals appear to have been heated under pressure. The nature of the final product as mined must depend on the character of the original deposits, and the conditions which prevailed throughout the different stages of the transformation. The assumption is that there is a gradual transformation of vegetable matter through the successive stages of peat, lignite, bituminous coal, and anthracite. Deposits are found representing all of the stages along this sequence.

The lignin theory of Fischer and Schrader states that in the decay of plant residues, the cellulose is altered and consumed by the action of the

bacteria. It disappears with the formation of carbon dioxide, methane, water, and water-soluble organic acids, such as formic and acetic acids, which are carried away by the water of the soil. The percentage of the aromatic lignin, on the other hand, increases with the increasing age of the peat. The lignins are transformed to humic acids, from which are then formed the alkali-soluble humus substances of brown coal, and finally the alkali-insoluble matrix of hard coal. The wax and resin-like materials of the plants, however, remain when the coal is formed and make up the bitumen. This paper is concerned chiefly with these waxes and resin-like materials as present in the different types of coals.

Other theories of the formation of coal have been advanced. The McKenzie-Taylor theory is of special interest for it states that the coal as mined is the end product, and the characteristics of each coal depend on the particular conditions which prevailed during the earlier stages of the transformation. For discussion in this paper the former theory has been considered satisfactory.

2. Composition of coal.

Wheeler¹ points out that all varieties of plants are built up of materials of but few general types, and hence from a chemical standpoint these plant materials are not so diverse as a botanical study might suggest. The proportions of these few types in the many plants do vary widely. The materials, as found in plants, do not retain their complex nature during the transformations previously described. Hence there are in bituminous coals three or four definite groups of compounds which may be traced to plants.

(1) Resins or waxes form a small part of most plants, but being resistant to normal bacterial decay, their proportion has increased in the coal.

(2) Protective tissues are the waterproof coverings of the plant parts,

such as spore exines and the cuticles of stems and leaves. These are also resistant to decay on account of the fatty substances they contain.

(3) Cellulose and lignin form the greater part of the plant. The former disappears to a large extent during bacterial decay. The remainder, with the lignin and the protein and carbohydrates in the cell contents, finally form complex brown products known as ulmins. These ulmins may be formed from different substances, yet they are all similar. Since these resultant ulmin compounds are the degradation products of the major portion of the plants, they constitute the bulk of the decayed mass from which coal is ultimately formed.

A banded characteristic of bituminous coal also exemplifies its composition. Stopes² has named these four visible ingredients vitrain, clarain, durain, and fusain. The former consists essentially of ulmin materials derived from the cellular structure of the plants. The durain is formed from mixed plant debris, rich in resistant protective tissues with a ground mass of ulmins similar, chemically, to those of vitrain. The clairain is intermediate between these two, while the fusain represents cell structures which have resisted bacterial decay, probably owing to an early aerobic decay, and now appear as opaque carbonised fibres.

Thiessen³ considers that all coals are essentially composed of two visibly different classes of compounds, - anthraxylon and attritus. The former comprises those constituents in coal which are derived from the woody tissues of plants, such as stems, limbs, twigs, and roots, and appears as homogeneous black bands. Attritus, which is of much duller appearance, consists chiefly of the more and most resistant plant products. A microscopic examination of peat attritus shows the following constituents: Humic degrada-

tion matter, spores and pollens, cuticles, resins, waxes, and opaque matter. The origin of this opaque matter has not, as yet, been definitely determined.

While the paleobotanist continues the microscopic examination to determine the constituents of coal, it is probable that the chemist can aid him to a considerable extent by a separation of the components with the aid of solvents.

3. Composition of the soluble portion.

It is possible to dissolve a portion of the coal by extraction with suitable organic solvents. The amounts and qualities of the extracts differ with the type of coal.

The bitumen as extracted from the brown coals or lignites may be said to consist generally of wax and resin-like substances present in the individual coals in varying proportions. From the waxes there have been isolated several acids, such as carbocerinic acid $C_{27}H_{54}O_2$, and montan acid, $C_{29}H_{58}O_2$, with the probability that acids of still higher molecular weight are present. They may be looked upon as normal fatty acids, for their melting points indicate that they are similar to known fatty acids having an odd number of carbon atoms. The alcohols esterified with the acids in the bitumen have been identified as tetrakosanol, $C_{24}H_{54}O$, cerylalcohol, $C_{26}H_{54}O$, myricylalcohol, $C_{30}H_{60}O$, and bituminol, $C_{32}H_{64}O$. From acid and saponification values, it appears that bitumen is a mixture of about 25 per cent free fatty acids, and 75 per cent real wax, the latter consisting of the esters of the fatty acids with the aliphatic alcohols. The resin-like portion of the extract has not been identified to a similar extent. There are indications, however, that it is made up of resinoleic acid resins. These are comparable with amber, and consist of free resinic acid, and resinic acid esterified

with resin alcohols. Quantitative but not qualitative differences are thought to distinguish the resins of bitumen from real earth resins.

The soluble constituents of a bituminous coal are known to consist, in part at least, of hydrocarbons and resins. The former are complex saturated (paraffin and naphthene) and unsaturated liquid hydrocarbons, with smaller quantities of solid paraffins and higher aromatic hydrocarbons. As yet, no relation has been found to exist between their quantity and the composition of the coal from which they are obtained. They are mainly derived, presumably, from the fatty oils and waxes of the original plants, none of which, however, survive as such in bituminous coal. The resins extractable are similar to the resin inclusions which can sometimes be separated mechanically from the coal.

The alkali-soluble constituents of coal are known as the ulmins. The amounts that can be extracted from coal varies from a negligible quantity from bituminous coals and anthracites to 60-70 per cent from lignites and brown coals. These compounds will not be considered in detail, as the chief interest in this investigation was the hydrocarbon, wax, and resin content of coals.

CHAPTER III.

REVIEW OF PREVIOUS WORK ON SOLUBILITY.

1. Early extraction with organic solvents.

The work done on the solubility of coal previous to 1850 was really of little significance, and by far the more important results have been obtained during the last thirty years. DeMarsilly observed (1862) that alcohol, chloroform, carbon disulphide, ether, and benzene acted as solvents on coal. It was noted that their action was much greater on coking than on non-coking coals. From preliminary experiments it was concluded that neither benzene nor chloroform was appreciably more effective as a solvent when the coal was treated under a pressure of fifteen atmospheres; that lean or anthracite coals were not affected by these solvents; and that coking coals, after treatment, did not yield as good a coke as they did before. Other workers of this period were: Guignet, Reinsch, Dondorff, and Smythe.

The work of Bedson⁴ (1900) caused considerable interest, for he noted that while ether, benzene, chloroform, light petroleum, and phenol, dissolved some constituents of coal, pyridine excelled all of these. He was able to dissolve 16-18 per cent of Durham coal, and 10-13 per cent of New Zealand coal by extraction with pyridine at temperatures of 117°-125°C. Baker⁵ continued Bedson's experiments using Soxhlet methods. He removed the last traces of the solvent by neutralization with hydrochloric acid, followed by filtration. It was noted that the percentage of hydrogen in the extract was greater than in the coal. Anderson and Henderson⁶ used pyridine as a solvent in investigations of coals from Bengal and Japan. They were able to entirely remove the caking constituents of the coal in this manner.

Stopes and Wheeler⁷ concluded that the work done previous to 1918

on the solubility of coals, proved that bituminous coals contain small quantities of resinous material extractable with organic solvents; that free hydrocarbons do exist in small quantities in coals; and that pyridine and other solvents afford a means of resolving many coals as an aid to the chemical examination of them. Although a great deal of the subsequent work was centered on the problem of determining the coking constituents of coals, this larger problem, namely the investigation of the chemical constitution of coal by a separation into its fundamental substances, was not lost sight of.

2. Extraction with neutral solvents.

Extraction. It was thought that a basic solvent, such as pyridine, might have some action other than one of solution, for example polymerization, in which case the materials found in the extract are not identical with the substances originally present in the coal. Hence there was a distinct movement towards the use of more neutral solvents such as benzene.

Bone¹⁰ (1922) published the results of the extractions of a number of coals. These coals had varying coking properties, the analyses showing a variation in volatile matter of 9.9 per cent to 32.2 per cent, and one special sample with a volatile matter of 53.8 per cent. The Soxhlet method was used at reduced pressures, in an atmosphere of nitrogen. The amounts of extracts obtained using benzene as the solvent varied from 0.66 per cent to 3.27 per cent, except in the case of the high volatile matter sample, from which 12.96 per cent extract was recovered. By using such solvents as ether, benzene, and alcohol, he was not able to entirely destroy the coking properties of the coals. This he did accomplish by extracting the coal with a mixture of pyridine and amyl alcohol. This latter extract, after the removal of the solvent, was refluxed with ether to dissolve the waxes and resins, which were

fractionated further with light petroleum. The fractions obtained were recognized as waxes, resins, and humic substances, the latter being non-resinous and chiefly of cellulosic origin.

Since it was impossible to entirely remove the coking constituents of the coal by extraction with neutral solvents at atmospheric pressures, attempts were made to extract the coal at higher temperatures. It should be noted that with increasing temperature, there is always the danger of some decomposition of the coal. Bone⁹ found that it was possible to heat samples of the Morwell coal from Australia, a brown lignite, to temperatures of 275°-375°C before any chemical change took place. Steam and carbon dioxide were given off above the decomposition temperature. Other experimenters verified the conclusions, that especially with higher grades of coal, no apparent decomposition occurred up to temperatures of 275° C.

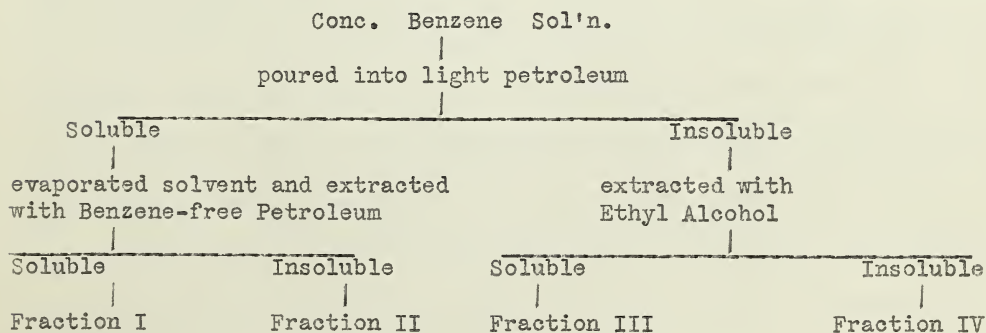
Fischer¹³, before beginning his work on the extraction of coal with benzene under pressure, had concluded that it was possible to heat the coal he was investigating to a temperature of 290°C without any appreciable decomposition. His extractions were carried out in an autoclave, which was continually shaken, and heat applied to raise the temperature to 285°C (55 atmospheres pressure). After several such extractions the coking properties of the coal were entirely destroyed, while the total yield of extract was much greater than the corresponding yield at low pressure. This extract was treated with petroleum ether, the soluble portion being a dark viscous oil, which was termed oil-bitumen, and the insoluble portion, a dark brown solid called solid bitumen.

The chief objection raised to the work of Fischer was that the coal was in actual contact with the extract in solution. A Soxhlet method which

permitted the use of high pressures was devised by Bone¹¹. The extractions were continued for a period of from 5 to 6 days, with the pressure gradually increased from 250 pounds to 500 pounds, and finally to 700 pounds (corresponding temperatures 240° - 260° - 285° C). There was no sign of any gas evolution as no residual pressure was noticed on cooling, although a small amount of water did appear after prolonged extraction. Hence it was concluded that no appreciable decomposition of the coal had occurred. By this process it was possible to obtain yields of 7 - 11 per cent from bituminous coals which only gave yields of 1.2 - 3.3 per cent extract at atmospheric pressure, and to entirely destroy the coking properties of the coal. The removal of the coking constituents was considered as indicating the completion of the extraction. Higher temperatures could not be used without considerable danger of some decomposition of the coal occurring.

On the extraction of several samples of semi-bituminous coals, only about 2 per cent was found to be soluble. The only brown coal extracted, from the Morwell deposits of Australia, yielded 15 per cent extract, but this extract was entirely different from the extracts obtained from bituminous coals.

Fractionation of the extract. The extract from bituminous coals was fractionated as follows:



Fraction I was in all cases a soft, non-nitrogenous, wax-or vaseline-like substance.

Fraction II was a reddish-brown solid of low melting point.

Fraction III was a reddish-brown, brittle, resinous substance.

Fraction IV was an amorphous, cinnamon-brown powder containing a small amount of sulphur and from 1.12 to 1.50 per cent of nitrogen. Bone concluded that the considerable amounts of nitrogen present suggested that these were the humic constituents of the coal, probably derived from an amalgamation of the protein and cellulosic transformation products.

The extract from the Morwell coal was, as stated, entirely different, and was, therefore, fractionated in a different manner. The fractions isolated consisted of a non-acidic and unsaponifiable resin portion; resin esters; aliphatic and alicyclic acid and ester portion; and a small amount of polyhydroxy phenols.

Attention might here be drawn to the controversy which developed as a result of the work of Bone and Fischer. The latter stated that the coking properties of the coal were due to the presence of the oil-bitumen, while Bone found that the humic bodies, Fischer's "solid bitumen", was mainly responsible for coking properties. Davis and Reynolds¹⁴ used Fischer's method for the extraction of Mesa Verda and Pittsburgh coals, obtaining about 8.5 per cent extract. They confirmed the results of Bone's work, namely that the solid bitumen was, in the main, responsible for coking properties. These same authors¹⁵ later verified their conclusions by the extraction of other samples. They also noted that as the extractions were continued, the extract became harder, that is, the proportion of solid bitumen removed increased with the duration of the extraction. On the cooling of the solution they detected the precipitate of a brown powder which they recovered by the filtration of the hot solution from the autoclave. This they termed "insoluble bitumen".

3. Montan Wax and its properties.

The manufacture of montan wax from certain German lignites is an important industry based on the extraction of coal by organic solvents. Redmayne¹⁶ describes the lignite as being distinctly woody, brown in colour, and of high moisture and volatile matter content. The seams are from 25 to 60 feet thick with light coloured bands indicating to some extent the richness. A seam of pyropissite, an almost white coal, was at one time worked which yielded 60 per cent bitumen on extraction. For a profitable recovery of the wax Redmayne considers that a laboratory extraction test of the seam must yield 10 per cent bitumen. In the commercial process the coal is heated in large conical tanks and a mixture of benzene and alcohol allowed to drain through it. The end point of the extraction is determined by noting the colour of the solution at the bottom of the tank. The solvent is recovered from the solution and the extract, after further drying, is cooled and bagged. The crude bitumen is dark coloured but it may be bleached either by steam distillation or by oxidation. However the crude form is used for many purposes.

Woods and Nicholas¹⁷ isolated montan wax from several samples of Nigerian lignites with the possibility of a similar utilization as their objective. The coals extracted were brown in colour, had a dull earthy texture, and appeared to contain "fine elastic particles". An analyses of these lignites showed a moisture content of about 20 per cent with a volatile matter of 49-56 per cent. It is worth noting here that no Canadian coals have such a high volatile matter content. An ordinary Soxhlet apparatus, jacketed with asbestos, was used throughout. Many solvents were tried, but benzene, toluene, xylene, butyl, and amyl alcohol, were found most suitable.

The results showed that butyl alcohol was the most efficient solvent, the yield of extract being as high as 22.4 per cent of anhydrous lignite, or 17.9 per cent of the original lignite. The benzene extraction resulted in the recovery of 12.6 per cent of the original lignite as montan wax.

The following table (Table I) shows the properties of montan wax and Nigerian wax as analysed by Woods and Nicholas.

T A B L E I.

	Nigerian Wax (crude)	Montan Wax (crude)	Montan Wax* (commercial)	Montan Wax (refined)
Melting Point °C	88 - 90	84 - 88	70.5-80.5	76
Acid Value	48 - 70	41.3	41.3	73
Saponification Value	140 - 185	140.5	138.9	73.9
Ester Value	80 - 125	99.2	97.6	0.6
Unsaponifiable Matter %	19.0	- -	- -	47.0
Iodine Value	46 - 48	48.7	40.9	- -

*This analysis is quoted by Woods and Nicholas from the work of Ryan and Dillon (Proc. Roy. Dublin Soc. 12, 1909-10, 202)

Hence the Nigerian wax compares very favourably with that from Germany. A high melting point and a high acid value are typical of montan wax. The melting point variation is probably due to the presence of acids other than montanic acid, esters of the acids of higher molecular weight, and hydrocarbons.

4. Extraction of Western Canada coals.

The extraction of a few Western Canada coals by Bone¹² are of particular interest. The method used with all of the samples was a high pressure extraction with benzene as a solvent, as briefly outlined on pages 11-12. The samples treated in this manner, as listed and classified by Bone were as follows:

1. Estevan, Saskatchewan - a brown coal
2. Alberta, non-coking, sub-bituminous coals.
 - (a) Cardiff - (Edmonton area).
 - (b) Rose Deer - (Drumheller area).
 - (c) Pembina - (Pembina area).
 - (d) Harlech - (Saunders area).
3. Canmore, Alberta - a semi-bituminous coal.

The extract from the Estevan coal resembled in many respects that from the Morwell brown coal, although the yield was but 4.5 per cent as compared to 15 per cent from the latter. The main difference in the extract was in the non-nitrogenous oil fraction, which in the Estevan sample was less oxygenated, and it also contained a smaller percentage of sulphur. This difference might be expected on account of the greater maturity of the coal.

The samples from Alberta were extracted for 50 hours at 33 atmospheres pressure (temperature -260°C) and then for a similar period at 40 to 48 atmospheres pressure (temperatures 270° to 285°C approximately). All the extracts were much the same, and resembled those from bituminous coals from other fields. The extracts were also fractionated according to the method devised by Bone given on page 12. The total yields and the amounts of each fraction obtained are shown in Table II. The results of the Estevan coal are included for comparison.

T A B L E I I.
Yields of Extracts and Fractions obtained by Bone from Alberta coals.

Coal	Total Extract %	Fractions			
		I	II	III	IV
1. Estevan	4.50	1.65	0.30	0.30	2.25
2. Cardiff	3.15	1.55	1.10	0.35	0.15
3. Rose Deer	3.85	2.20	0.70	0.75	0.20
4. Pembina	3.85	1.50	1.45	0.60	0.30
5. Harlech	4.30	1.30	1.30	1.20	0.50
6. Canmore	1.35	1.20	0.10	0.02	0.03

Fraction I was in each case a semi-solid or vaseline-like, non-volatile, dark red-brown, non-nitrogenous substance. On analysis it was similar to the Fraction I from English bituminous coals, although it contained less oxygen.

Fraction II was always a chocolate-brown, amorphous solid.

Fraction III was an amorphous, brittle substance of resinous appearance.

Fraction IV was an amorphous, brown solid. Only a small amount of this fraction was present in any of the samples extracted.

The Canmore coal, on extraction, yielded but 1.35 per cent extract, nearly all of which was Fraction I. This was an oil rather than a wax, and contained a trace of diphenyl. It was suggested that under the stress of mountain building, the materials normally found in Fractions II to IV were destroyed.

These results are of interest as they are comparable with those obtained by the writer and described later in this paper. The samples used by Bone are far from representing all the grades of Alberta coals, and no ^{suggestion} ~~reference~~ is made as to ^{any} ~~the~~ similarity of the extracts obtained to the montan wax extracted from the German lignites.

Use of phenol as a solvent.

The extraction of coal with phenol has not received the same investigation as has that with either benzene or pyridine. There is an obvious danger that an acid solvent may react with some of the constituents of the coal and change their character. The same objection has been made to the use of pyridine on account of its basic properties. The latter, however, has in the majority of cases, proven more efficient than phenol, and has been favoured. Either of these solvents will extract a much larger fraction of the coal than will benzene. Therefore lower temperatures can be used and the danger of thermal decomposition of the coal is reduced.

Frazer and Hoffman¹⁸ extracted a sample of Illinois coal with phenol by heating it to a temperature of 140°C, the coal being in actual contact with the solution containing the extract. They obtained a yield of 10.8 per cent extract on the ash and moisture free basis. They fractionated this extract into many portions, which were presumed to be specific compounds, although they were not able to definitely identify them. They stated their intention to use pyridine in subsequent extractions in the attempt to determine the chemical constituents of coal.

Parr and Hadley¹⁹ investigated the solubility of coal, and tried many solvents. They finally arranged them in the following order of efficiency: Phenol, ortho-cresol, low boiling tar distillate, para-cresol, pyridine, phenol-toluene mixture, aniline, methyl aniline, acetone, toluene, benzene, carbon disulphide, and turpentine. Some of these seemed to undergo decomposition during extraction, while others were not very effective. They concluded that phenol was the best solvent for extraction purposes. The extraction cone was suspended in a Kjeldahl flask, in which was placed the solvent. The flask was fitted with a rubber stopper, through which passed a tube containing toluene, this tube being attached to a reflux condenser. The phenol condensed on this tube of toluene at 110°C, the boiling point of toluene, and dropped back into the extraction cone. All of the extractions were done in an atmosphere of carbon dioxide to prevent any oxidation. Their results ranged from 40 per cent extract from coals with high volatile matter to 20 per cent extract from coals with low volatile matter. They found that some decomposition of the phenol does occur with prolonged boiling, but the residue so formed does not amount to more than 15 milligrams from 50 ccs of the solvent. The weight of the extract and of

the residue together very nearly equalled the weight of the original coal, from which they concluded that there was but a negligible decomposition of the coal, if any.

It is quite evident from these results that phenol dissolves a much larger fraction of the coal than does the neutral solvent benzene. If any examination of the extract was planned, care would have to be taken to prevent any oxidation. The statement of Parr and Hadley that phenol is more efficient than pyridine does not agree with the findings of most other workers, notably Wheeler and other European investigators. This suggests that U.S.A. coals may differ in this respect from European coals.

Use of pyridine as a solvent.

Pyridine has been a very popular solvent for the treatment of coal, as it was early established that it would entirely remove the coking constituents of coal. The suspicion that it might act as a reagent as well as a solvent has of late been disproven to the satisfaction of Wheeler and his co-workers. It is quite generally accepted that its chemical action, if any, is very slight. Stopes and Wheeler²⁰ in reviewing the work done with pyridine up to 1924, point out that commercial pyridine is not satisfactory as a solvent for it contains interfering impurities, including a considerable portion of pyridine hydrate, which lessens its solvent power. The coal used, moreover, must be carefully dried previous to extraction to prevent the formation of this hydrate.

Although pyridine had been used as a solvent for some time, Clarke and Wheeler²¹ (1913) were the first to treat this extract with chloroform thereby separating it into two fractions. These were termed the gamma or resinic bodies, soluble in chloroform, and the beta cellulosic bodies, insoluble in chloroform. Illingworth²² from investigations of the effect of

heat on coal, concluded that the decomposition which occurred with gradually increasing temperature resulted in the destruction of the pyridine soluble fractions, and was more rapid for the beta cellulosic than the resinic portion thereof. He later suggested that the plasticity of coal was due to the resinic fraction of the extract, the degree of plasticity depending on the amount of resin present, the melting point of these resins, the temperature to which the coal is heated, and the proximity of this temperature to the point of decomposition of the resins.

Later Cockram and Wheeler²³ resolved the gamma or resinic portion into four other fractions by the use of light petroleum, ethyl ether, and acetone. The fraction soluble in light petroleum was 33 per cent of the total and consisted chiefly of saturated and unsaturated hydrocarbons, with about 20 per cent resins. That fraction of the residue soluble in ether was 37 per cent of the total and consisted of a saponifiable portion, phenols and hydroxy acids in the form of esters, and an unsaponifiable portion, a dark-red solid made up of resins and resin degradation products. The other two fractions were very similar with the exception of their solubility in acetone, and were termed resin-like substances.

From further investigation of the same coal as before but with benzene as a solvent, these authors concluded that a temperature of 285°C would be necessary to remove the same amount of extract. The extract so obtained differed from that of the pyridine extraction, particularly in regard to the amount and the properties of the various fractions. The "humic" fraction isolated by Bone contained in their opinion 30-45 per cent resins. From this and other results they concluded that thermal decomposition of the coal does occur at the temperatures employed with benzene, so that pyridine is much the more suitable solvent.

Bone⁸ (1919) concluded from experiments that pyridine does act other than as a solvent on some constituents of coal. He found the pyridine would become coloured if allowed to remain in contact with the fully extracted coal residue. To confirm the conclusion, he heated the coal with pyridine in a closed tube to 130 - 150°C and found the yield of extract on subsequent extraction was larger than that from the original coal.

Hence there has been considerable controversy over the relative values of benzene and pyridine as a solvent for the treatment of coal. Although none of the Alberta coals received were extracted with pyridine, the writer is of the opinion that such might appropriately be the next stage in the investigation.

The rational analysis of coal.

One of the results of the successful extraction of coals by bituminous solvents has been the suggestion that a new analysis of coal be adopted to determine both its character and its classification. This is termed "The Rational Analysis of Coal".

Wheeler¹ points out that to express the composition and quality of coal, it is necessary to know the amounts of hydrocarbons and resins, the resistant plant entities, and the ulmin compounds that it contains. The hydrocarbons and resins are those portions which are soluble in suitable organic solvents. The above writer favours the use of pyridine for a complete extraction of these substances from the coal. The resistant plant entities are the spore exines, cuticles, and woody tissue which have resisted bacterial decay and are present in the coal. They remain as the insoluble residue when coal is carefully oxidized and the alkali soluble

constituents are removed. They may form as much as 20 per cent of a band of durain, while vitrain contains a negligible quantity. The chief properties of this fraction are their resistant power to decay and oxidation, and the high proportion of tar they yield on destructive distillation. The ulmin compounds are recovered by neutralizing the alkaline solution in which the coal was oxidized. They are dark-brown colloids resembling the peat ulmins, but they have a higher carbon content and are more definitely acidic. These ulmins when first formed are soluble in alkali, but as the coalification proceeds, the content of soluble ulmins in the coal decreases, and they become more difficult to regenerate by oxidation. Hence this latter property may be used to indicate the grade of the coal.

Francis and Wheeler²⁴ measure the reactivity of the ulmins with oxygen, and conclude from their results that this property indicates the degree of coalification better than does the carbon content.

Thiessen and others favour the microscopic examination of coal in order to determine its constituents. Many of these constituents may be recognised, but the quantitative determination of them seems impossible by this method. One decided advantage is that there is no danger of any chemical action which might change the constituents, due to the presence of the solvent, or the temperatures employed in the extractions of the various fractions. A combination of the two methods suggested might eventually make possible a classification of coal on this basis.

CHAPTER IV.

EXPERIMENTAL.

1. Extraction at normal pressure.

Preliminary experiments. The primary idea of this investigation was the possibility of finding some Alberta coal with a high montan wax content. This suggested the use of benzene, and a mixture of benzene and alcohol as solvents. More broadly, the object was to examine the relative solubilities of a number of coals, rather than to compare the effect of a number of solvents, so selected solvents could be used. It was suggested, therefore, that the initial work be done with the more common neutral solvents, such as benzene and xylene. These were immediately available and their cost was not excessive. To avoid the danger of thermal decomposition of the coal, it was decided to attempt first, the extractions with these solvents at atmospheric pressure. Most of the low pressure extractions were done with coal from the Penn mine at Edmonton, although a few samples of other coals were at times treated.

A method employing the Soxhlet principle was chosen, as it allowed continuous extraction. The ordinary Soxhlet, as devised for the extraction of fats, was unsuitable for the yields were not expected to be over 10 per cent, and the amount of coal which could be treated would be much too small.

The first apparatus designed consisted of a brass cup 14 inches high and 2 inches in diameter, closed at one end. A $\frac{1}{2}$ inch copper tube led ~~from the bottom~~ ^{outside} of the cup to within 3 inches of the top, and then to a litre flask which contained the solvent. A fine copper screen covered with a thick layer of glass wool, was placed in the bottom of the cup. About 200 grams of air dried coal from the Edmonton area, ground to pass a 28 mesh sieve, were placed

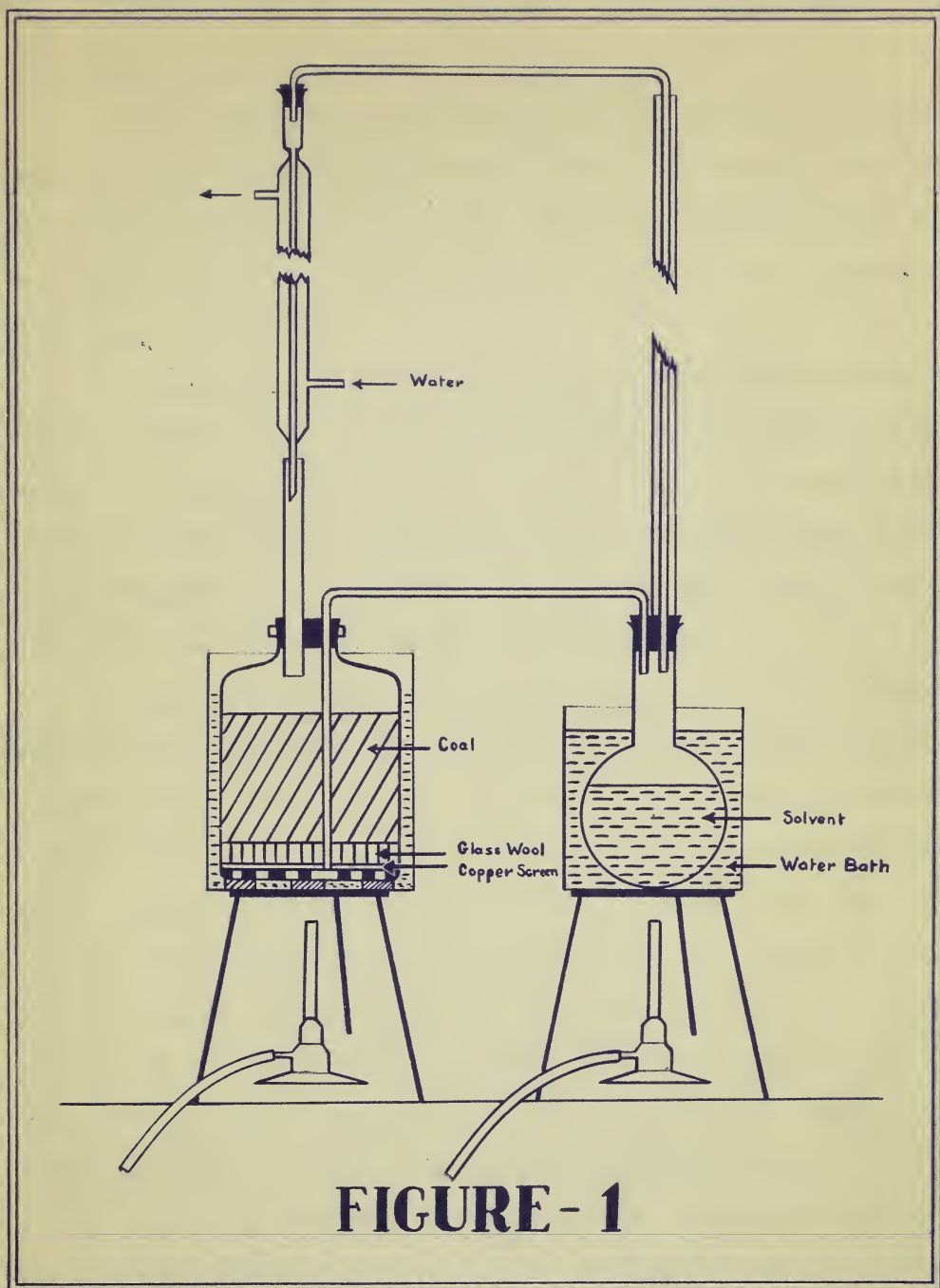
in the brass cup as described, and covered with benzene. Five hundred cc. of the solvent were placed in the litre flask and heated by a water bath. The vapour was condensed in a water condenser, and the liquid led into the top of the extraction cup through a loosely fitted cork stopper. As the level of the solution in the cup rose above the top of the small tubing, that part of the solution which had passed through the whole column of coal siphoned into the flask. Thus the extract remained in solution in the flask while the solvent was used again. Extraction at as high a temperature as possible at atmospheric pressure, was insured by immersing the extraction chamber containing the coal, in a water bath kept at a temperature close to the boiling point of the solvent. It was not feasible to run the apparatus at night due to the necessity for the careful regulation of heat, and the danger of fire. Under these conditions the extraction took two weeks before the solution siphoning over became quite colourless. The actual period of extraction was estimated to be 120 hours.

Examination of the solution in the flask at the end of the extraction showed the presence of a fine brown precipitate. This was at the time, thought to be coal which had been carried over on account of imperfect filtration by the screen and the glass wool, and was therefore filtered off. Part of it, at least, was probably similar to the insoluble bitumen described by Davis and Reynolds¹⁵ in a later publication. The solution after filtration, was concentrated, transferred to a weighed beaker, and the remainder of the solvent removed by heating in an oven to 125°C. No special care was taken to prevent oxidation, as the aim of this experiment was only to determine the suitability of the method for the examination of the coals along the lines planned.

The extract was a solid, dark brown in colour, with a distinct bitumen odour. The yield was but 0.78 grams, or 0.39 per cent of the original sample. Hence it was concluded that either the coal did not contain an appreciable amount of benzene-soluble constituents, or that extraction at higher pressure was necessary to remove them.

Before deciding that the latter was necessary, an apparatus was devised which permitted the extraction of a much larger sample of coal. A large glass bottle which would hold about one kilogram of coal was secured and the apparatus set up as shown in Figure I. The cork stopper of this flask was made air-tight by a liberal covering of litharge and glycerine paste, and DeKhotinsky Cement. This was necessary as the level of the siphoning tube was above the top of the bottle. The glass tube fastened into this stopper was made about 18 inches long. The condensed solvent, rising in this tube created a sufficient head or pressure to insure the siphoning of the solution from the extraction chamber to the litre flask. The extraction chamber was immersed in a water bath, the temperature of which was kept at 80°C. The main advantages of this apparatus over the previous one was that a much larger sample of coal could be treated, and since all the parts were made of glass, it was possible to watch the extraction more closely.

A sample of Hillcrest coal was taken for the first extraction. About 1200 grams of the air-dried coal were ground to pass a 28 mesh sieve, placed in the large glass bottle and extracted with benzene. The extraction was considered completed at the end of two weeks since the solution then siphoning over was quite colourless. The solution was removed from the flask, filtered and concentrated. The last traces of the solvent were removed by



heating in the oven as before. The yield was 2.37 grams, or 0.2 per cent of the original coal.

The residue from this extraction was then treated with xylene for two weeks and a further 0.1 per cent extracted. This indicated that xylene was probably a more efficient solvent. However, neither benzene nor xylene were considered efficient enough for general use in the investigation if this method was to be followed.

A sample of the Morwell coal from Australia, which had been stored in the Industrial Research Laboratories for some time was treated in this manner for two weeks with benzene. The yield from this coal was 1.7 per cent of the air dried sample. An extraction of this coal with benzene under pressure by Bone (page 12) yielded 15 per cent extract. Hence it was concluded that the method employed was not satisfactory.

Reduction of the coal during extraction. The yield of extract obtained by a benzene-pressure extraction of bituminous coals, according to the literature, varies from 7 to 12 per cent. Hence it was suggested that reduction of a lignite coal during extraction might appreciably increase the yield obtained. Assuming that some reduction is accomplished, the extract obtained would probably more closely resemble that from bituminous coals than does the extract of the original coal. Similarly the oxidation of a lignite previous to, or during, extraction, might increase the yield as many immature coals, such as those of Germany and Nigeria, contain a much larger benzene-soluble portion than does the lignite from the Edmonton area.

Therefore sulphur dioxide, dried by passing through sulphuric acid, was allowed to bubble through the solvent covering the coal in the extraction chamber. Both benzene and xylene extractions of the coal from the Edmonton

area were made in this manner. It is questionable if any reduction did occur, for it seems probable that a much higher temperature than that of the extraction chamber, namely 80°C, would be necessary. The results of these extractions were as follows:

<u>Solvent</u>	<u>Yield % (air-dried coal)</u>
Benzene	0.13
Xylene	0.16

These yields were of the same order as those obtained previously from this coal. Hence it was concluded that either no reduction occurred, or that such reduction has no effect. However, the method was considered unsatisfactory and this point, as well as the effect of oxidation, was left for further consideration.

2. Extraction at High Pressure.

Preliminary experiments. The initial objection to the extraction of coal at high pressures was the increased danger of some chemical action between the coal and the solvent, and the thermal decomposition of the coal itself. The pressures used previously were, as described, equivalent to temperatures up to 285°C. It was thought that an appreciable amount of the coal might be soluble at much lower pressures, and any chemical action that might occur would be decreased. In point of fact, the autoclave available did not permit the use of very high pressures.

While no attempt was made to prove that no decomposition of the coal did occur at the temperatures employed in the methods described below, it was noted that there was no sudden increase in pressure during extraction. Such increase would probably be the result of any serious decomposition, due to the formation of such gases as the oxides of carbon and the hydrocarbons of the

of the methane series. Decomposition would also be evidenced by a residual pressure in the autoclave after cooling, but this was not found to be the case in any of the extractions made. Again, Mr. K. C. Gilbert of the Industrial Research Laboratories, in investigating "The Coking Properties of Coal", (M. Sc. thesis, 1928), proved that good coking coals show little decomposition, as measured by the volume of gas given off, up to temperatures of 400°C, and that poorer coking coals may be heated up to 325°C. without any material decomposition of them. Hence it was assumed that no decomposition occurred during any of the extractions described below, where the temperature never rose above 225°C.

Many of the earlier extractions at high pressures, by other workers, were done by the intermittent method, with the residue in actual contact with the solution containing the extract. The autoclave designed by Bone¹¹ works on the continuous Soxhlet principle, but was costly. A simpler and less expensive apparatus was devised for this work, and satisfactorily achieved the same end. A gas heated autoclave of 3 litres capacity, fitted with a pressure gauge, thermometer well, safety valve, and an adjustable escape valve was obtained. A copper cup, the diameter of which was about 2 inches less than that of the reaction chamber, was supported therein on a bed of silica (Ottawa sand), as shown in Figure 2. A smaller copper cup, 6 inches high and 4 inches in diameter, was suspended by copper wire inside this larger cup. A thermometer well, of sufficient length to reach the bottom of the inner cup, was inserted. The lower part of the well, that is that part inside the cup, was enclosed by a brass tube $1\frac{1}{2}$ inches in diameter, open at both ends. This tube extended above the cup as shown. The autoclave and cups were thoroughly cleaned by heating them with fresh portions of benzene until the solvent re-

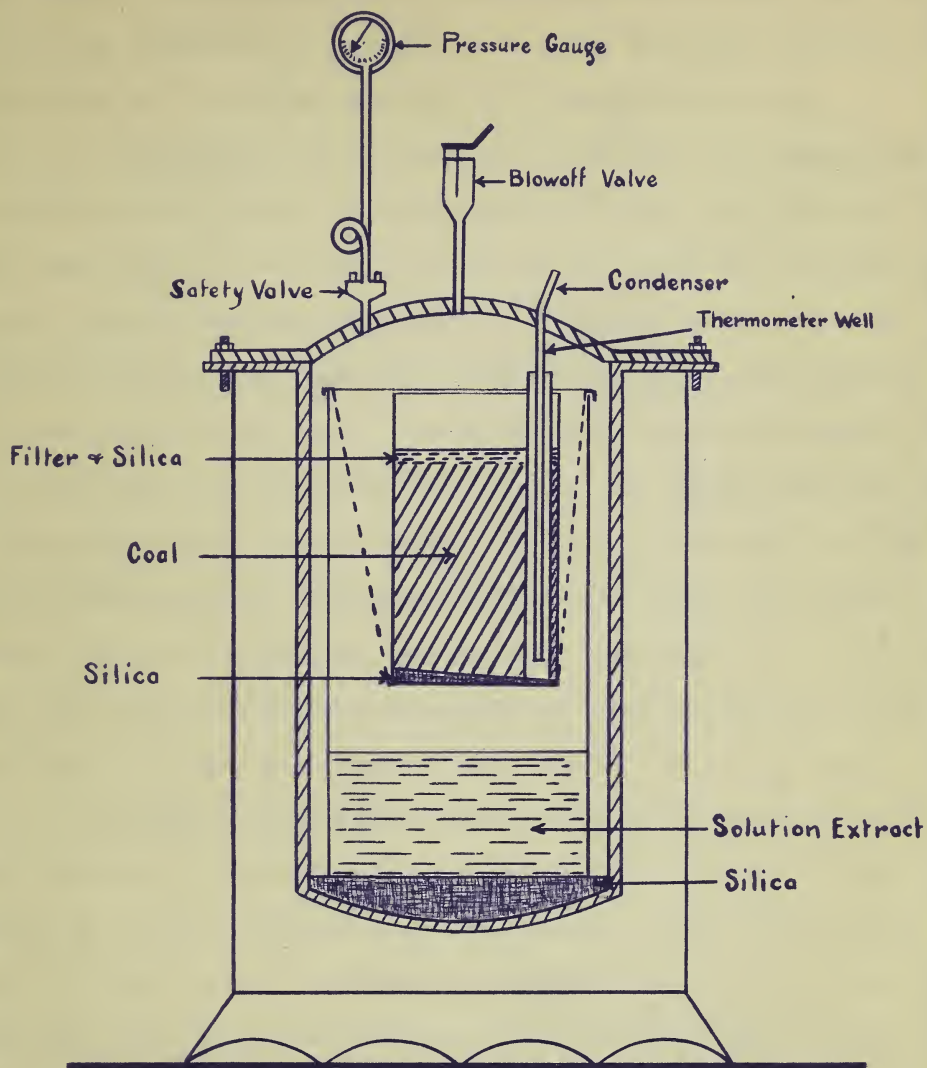


FIGURE - 2

moved was nearly colourless. The sample of coal was placed in the inner cup, and entirely covered with a filter paper weighted down with sand. About 2400 cc. of the solvent were then added, care being taken that the level did not rise above the top of the inner cup which contained the coal.

In operation the autoclave was heated until the desired pressure was registered on the gauge. The thermometer well was cooled by a current of cold air blown into it. The vapours of the solvent, therefore, condensed on this cooler surface, and the liquid ran down the inside of the brass tube to the bottom of the cup, and then rose up through the coal. After removing the soluble portion from the coal, the solution was filtered through the filter paper and sand, and overflowed into the outer cup. Hence the solution containing the extract remained in the outer cup, out of contact with the residue, and the extraction was continuous. The air cooler was later changed to a water cooler, as it was found on opening the autoclave that the coal was quite dry. The completion of the extraction could only be determined by opening the autoclave and noting the colour of the solution in the inner cup.

A sample of the Morwell brown coal was extracted with benzene using this apparatus. The yield of extract was 4.6 per cent. On a second extraction, a yield of 3.7 per cent was obtained. Unfortunately these results were of little value as considerable difficulty was experienced with the autoclave, and the pressure was by no means constant. When compared with the yield of 1.7 per cent extract obtained by the extraction of this coal at atmospheric pressure, they did indicate that a much larger portion of the coal was removable with benzene by increasing the temperature.

A sample of Edmonton coal was ground to pass a 28 mesh sieve and placed in the cup. Finer grinding might have accelerated the extraction, but it was not feasible for it prevented the rise of the solvent through the coal. It was decided to limit the pressure to 250 to 275 pounds (corres-

ponding temperatures 210 - 215°C). An increase to 300 pounds pressure would have increased the temperature but 10°C, and it was difficult to keep the autoclave gas-tight at higher pressures. It was assumed that the extractions were made at a temperature of approximately 200°C, as the condenser would lower the temperature in the inner cup. This was roughly confirmed by rapidly removing the water cooler, and placing a thermometer in the well. It was not thought necessary to standardize the pressure gauge for with gas heating, and the conditions under which the experiments had to be conducted, it was impossible to avoid pressure variations up to 25 pounds. The extractions could not be made through the night on account of the danger of fire, but since the coal was at all times covered with the solvent, it is improbable that this made any difference. After 24 hours actual extraction of this sample of Edmonton coal, the solution in contact with the coal was quite clear. The solution was therefore removed and filtered. It was carefully concentrated and the remainder of the solvent removed by heating in the oven at 125°C. During this final heating a current of natural gas was passed over the extract to prevent any oxidation. The yield of extract was 1.7 per cent which compares favourably with the yield of 0.4 per cent from the same coal at atmospheric pressure.

Since one of the factors governing the efficiency of a solvent for coal is its miscibility with the water present in the coal, it was thought that a mixture of benzene and alcohol might give better results. The addition of even a small quantity of alcohol to benzene materially increases the solubility of water therein. Another sample of the Edmonton coal was therefore treated with a mixture of three parts of benzene to one part of ethyl alcohol, under the same conditions as described above. The yield of extract was 1.9 per cent, a slight increase over the previous yield of 1.7

per cent. Since experimental errors might be as high as 10 per cent, it is questionable if this increase were due to the alcohol. However, it was decided to continue the extractions with the mixture of solvents, but substituting methyl alcohol for the ethyl alcohol on account of the lower cost. Again this mixture is used in the extraction of the German lignites, as the average moisture content of the coal in the extractors is from 13 to 15 per cent. The montan wax content of Alberta coals was of special interest in this work.

Considerable difficulty was experienced in the concentration of the solutions removed from the autoclave. The most satisfactory method of applying heat was an oil bath as temperatures of 120°C were required to concentrate the solution to less than one litre. At this concentration it was advisable to continually shake the flask to prevent sudden ebullition. Passing a small current of natural gas through the solution while heating was also helpful. The flask was raised from the oil bath as the level of the solution was lowered to prevent the extract hardening on the walls of the flask. The advisable end point of the concentration could be judged by noting the sluggishness of the solution. The time required for each concentration was from 3 to 5 hours.

The standardized method. The method for comparative work on the coals to be tested was standardized as follows.

The sample, as received, was air-dried and ground to pass a 28 mesh sieve. Exactly 700 grams of this sample were placed in the inner cup, the bottom of which was covered with sand to facilitate the flow of the solvent into the coal. The sample was then covered with a tight fitting filter paper weighted down with about half an inch of sand. The cup was placed inside the larger cup in the reaction chamber, and $2\frac{1}{2}$ litres of the

mixed solvent added. Sufficient solvent to cover the coal was placed in the inner cup in order to prevent any danger of the coal becoming caked before enough had been condensed to cover it. Heat was applied gradually until the pressure rose to 250 pounds (temperature 210°C), and adjusted to keep the pressure as constant as possible. The extraction was continued for a total of 24 hours heating, and then, after cooling, the contents of the inner cup were examined. If the solution in contact with the coal was colourless, the extraction was considered completed. In only one case, which is noted in the subsequent table (Table 5) was a longer period required for the extraction.

The solution was removed from the reaction chamber and filtered. The latter was necessary for some of the sand and coal became mixed with the solution in removing the solvent from the inner cup. The solution was then concentrated to less than $\frac{1}{2}$ a litre. While hot, the concentrated solution was poured into a previously weighed bottle, fitted with a suitable stopper.

The distilling flask was washed with two 10 cc. portions of fresh solvent and the washings added to the solution. The bottle was then placed in the drying oven and the temperature gradually raised to 125°C. A stream of natural gas was passed through the bottle to prevent any oxidation, and to assist in the removal of the solvent. The extract was left in the oven for at least two hours after the odour of the solvent had disappeared. In one or two cases it seemed impossible to entirely rid the extract of this odour. Heat was applied for at least 8 hours in these cases, and not more than traces of the solvent could have remained, for these and all other extracts became liquids, even though viscous ones, at the maximum temperature. The bottle was then removed from the oven, tightly stoppered, allowed to

cool, and weighed. Reheating did not cause any perceptible change in the weight.

Samples and their proximate analyses. Since it was not feasible to extract even one sample from each of the various coal areas of Alberta, due to lack of time, it was necessary to select a number of them. In making this selection it was arranged to secure samples of the three grades of coal, namely bituminous, sub-bituminous, and lignite, and then from the districts selected it was desired to sample the highest volatile matter coal that could be obtained. It might be again pointed out that both the German and the Nigerian lignites have a very high volatile matter content. Also Wheeler, Bone, and others, have noted that the yield of extract from bituminous coals, in general, varies directly with the volatile matter content of the coal.

Unfortunately all of the samples selected could not be obtained, as some of the mines were inaccessible during the winter months. This is particularly true of the mines from which the immature coal is obtained, as little coal is taken from them. Through the courtesy of the Mines Branch of the Provincial Government, the following samples were received.

T A B L E I I I .

COALS USED FOR SOLUBILITY TESTS.

Area (Horizon)	Mine (Grade of coal)	Location	Owners
1. Edmonton (Edmonton)	Chinook #147 (Domestic)	River Lot #20 Edmonton	Penn Coal Co. Edmonton
2. Drumheller (Edmonton)	Western Gem #678 (Domestic)	10-29-20 W 4	Western Gem Coal Co. Drumheller
3. Gleichen (Edmonton)	Costella #1265 (Domestic)	11-25-22 W 4	Hans Costella Standard

Table III - continued.

Area (Horizon)	Mine (Grade of coal)	Location	Owners
4. Coalspur (Belly River)	Mercoal #846 (Sub-bituminous)	25-48-22 W 5	McLeod River Collieries.
5. Lethbridge (Belly River)	Wall #1020 (Sub-bituminous)	7-7-21 W 4	Cox and Paris, Raymond
6. Crowsnest (Kootenay)	Christie #295 (Bituminous)	10-5-1 W 5	B. A. Wilson Pincher Creek
7. Crowsnest (Kootenay)	Beaver #199 (Bituminous)	3-6-2 W 5	Smith Brothers, Beaver Mines
8. Mountain Park (Kootenay)	Mountain Park #282 (Bituminous)	33-45-23 W 5	Mountain Park Coll. Mountain Park
9. Mountain Park (Kootenay)	Luscar #905 (Bituminous)	23-47-24 W 5	Luscar Collieries Luscar
10. Crowsnest (Kootenay)	Coleman #88 (Bituminous)	16-8-4 W 5	International Coll. Coleman
11. Estevan, Saskatchewan (Brown lignite)			Western Dominion Coll. Taylorton, Sask.

The Mountain Park, Luscar, and Coleman samples were the fines separated for washability tests.

The Christie and Beaver coals were selected as two coals from the Kootenay horizon just on the edge of the boundary separating the Kootenay and Belly River formations. It was hoped to obtain one or more coals just across the boundary line in the Belly River formation, such as the Lundbreck coal, where some of the coals are fair coking coals.

The samples were of the average mine run and no attempt was made to prevent air drying or oxidation during transit. Subsequent reference to these coals will be made by naming the mine from which they were obtained.

A proximate analysis of each of the above coals was made by the standard methods as outlined in Bulletin 14 of the Scientific and Industrial

Research Council of Alberta. The results of these analyses are shown in Table IV.

T A B L E I V.

PROXIMATE ANALYSES OF COALS TESTED.

	Moisture %	Ash %	Volatile Matter %	Fixed Carbon %	Volatile Matter (ash free dry basis) %
1. Chinook	16.8	6.5	34.5	42.2	44.9
2. Western Gem	14.8	8.9	32.0	44.3	41.9
3. Costella	14.0	10.4	32.5	43.1	43.0
4. Mercoal	5.4	8.6	37.4	48.6	43.5
5. Wall	7.5	12.6	34.9	45.0	43.7
6. Christie	1.7	9.4	31.8	57.1	35.8
7. Beaver	0.9	12.2	30.9	56.0	35.5
8. Mountain Park	1.0	10.6	30.8	57.6	34.8
9. Luscar	0.6	5.1	27.1	67.2	28.7
10. Coleman	0.6	13.5	25.4	60.5	29.6
11. Estevan (Sask.)	16.6	6.8	33.9	42.7	44.3

The volatile matter on the ash-free basis was calculated for the above coals.

Results of benzene-alcohol extractions. The samples received were extracted with a mixture of benzene and alcohol by the standard method previously outlined. The results are shown in Table V. The yields have also been calculated to a percentage of the ash-free dry coal.

In only one case, namely the extraction of the Mountain Park sample was it necessary to continue the extraction for a period longer than 24 hours. At the end of 48 hours extraction, however, this sample was considered completely extracted. A check extraction of this sample also required 48 hours

heating, but the yield was only 9.7 per cent of the original coal. This indicated that the yields are only approximate, the experimental error being as high as 10 per cent. This might be accounted for to some extent by the difficulty in keeping the pressure constant in the autoclave used.

T A B L E V.

RESULTS OF BENZENESALCOHOL EXTRACTIONS OF COALS

Sample	Yield of extract	
	% original coal	% ash-free dry coal
1. Chinook	1.9	2.4
2. Western Gem	3.8	5.0
3. Costella	3.1	4.1
4. Mercoal	4.9	5.7
5. Wall	8.5	10.6
6. Christie	2.2	2.5
7. Beaver	8.5	9.6
8. Mountain Park	10.9	12.5
9. Luscar	0.3	0.3
10. Coleman	1.6	1.9
11. Estevan	2.7	3.5

Extraction of the treated coal. The possibility of materially increasing the yield of extract by reduction or oxidation of the coal previous *extraction has been discussed. The earlier attempt to increase* the yield by passing a current of sulphur dioxide, a reducing agent, through the solvent and the coal during extraction had not been successful. A similar treatment using this method of extraction was impossible on account of the pressures used. Therefore it was decided to treat the coal previous to extraction.

Reduction. An iron cylinder which fitted a muffle furnace was

partly filled with a weighed amount of the Chinook coal. Caps, padded with asbestos, were fastened to each end of this cylinder and connections were made with the front end to permit the passage of a stream of hydrogen through the coal. The temperature of the furnace was increased very slowly reaching a maximum of 375°C in two hours, and was held there for a half an hour, a liberal stream of dried hydrogen passing through the coal during the whole period. The coal was allowed to cool in this reducing atmosphere, removed from the cylinder, and weighed. This treated coal was then extracted with the benzene-alcohol mixture according to the standard method. The results are as follows:

Weight of coal previous to heating	660 grams	
" " after heating	512 "	
Loss in furnace	148 grams	= 22.4% original coal
Original moisture in coal		16.8%
Difference		5.6%

Yield of extract 11.5 grams 1.8% original coal.

This yield can be compared with the 1.9 per cent extract found in the regular test with the untreated coal.

The difference of 5.6 per cent shown in the above results does not necessarily signify that reduction had occurred. There would in all probability be some loss of the volatile matter of the coal at the temperature at which the coal was treated. It was noted, however, that steam escaped from the outlet tube in appreciable quantities even after two hours of heating, although it had practically ceased when the heat was removed. As the amount of extract obtained from the coal was the same as that from the untreated coal, it did not seem worth while to determine by means of ultimate analyses the extent of reduction effected.

Oxidation. An attempt was made to oxidize the coal previous to

extraction. The sample of the Chinook coal was placed in an open dish in a well ventilated oven, the temperature gradually raised to 130°C and held there for $1\frac{1}{2}$ hours. Higher temperatures resulted in the ashing of an appreciable amount of the coal. The sample was then extracted with benzene and alcohol in the autoclave. The results were as follows:

Weight of coal before heating	600 grams	
" " after heating	474 "	
Loss in oven	126 grams	21.0% original coal
Original moisture in coal		16.8%
Difference		<u>4.2%</u>
Yield of extract	8.8 grams	1.5% original coal

Again the difference of 4.2 per cent was not necessarily due to oxidation of the coal. In fact a mild oxidation of the coal might result in an increase in weight, allowing for the loss of moisture on heating. The above decrease might be accounted for by either a more complete dehydration of the coal than is obtained in the ordinary moisture determination, or by excessive oxidation of the coal resulting in some of the constituents being ashed. Instead of a desired increase in the yield of extract, there was a decrease, hence there seemed to be no object in making ultimate analyses to determine the extent of oxidation effected.

It might be pointed out that the coal could have been subjected to a much more vigorous reduction or a milder oxidation. The value of such treatment, if it were successful in increasing the yield of extract on extraction with organic solvents, would appear to be in its commercial applications. No costly treatment of the coal would be profitable unless the yields were considerably greater, or the extract were to become more valuable than at present. As the tests showed, if anything, decreased yields with no noticeable change in the nature of the extract, it did not appear worth while to continue this branch of the work.

The results of these experiments conform with the current opinion in regard to the constituents of coal. Hydrocarbons and resins are considered to be among the constituents more resistant to bacterial decay and oxidation. The reduction and oxidation as carried on in the tests would probably effect the other constituents in the coal, and not the extractable bitumens.

3. Phenol Extractions.

Preliminary. It was desired to investigate the solubility of some Alberta coals in a solvent distinctly different from the neutral ones already employed. Of the solvents which are mentioned in the literature, phenol and pyridine held the greatest promise. Phenol was finally chosen because it was readily procurable and comparatively inexpensive, and pyridine, if used, must be chemically pure. Parr and Hadley¹⁹ found that phenol was the best solvent for the examination of U.S.A. coals, and Alberta coals resemble these rather than the European coals which Wheeler and others have investigated. The presence of impurities in pyridine, and particularly pyridine hydrate, decrease its solvent power. It was considered impossible to dry the coal sufficiently, previous to extraction, to prevent the formation of this impurity during the extraction.

Previous discussion has established the fact that Soxhlet methods are preferable when possible, for the extraction can then be continuous. Several extractions of the Chinook coal were made using Kjeldahl flasks as the extraction chamber, the extraction cone containing the coal being supported above the solution by a wire frame which rested on the bottom of the flask. An alundum extraction cup could not be used, for the pores were readily plugged by the finely ground coal. A paper extraction thimble was also unsatisfactory, for on cooling the solidification of the phenol broke the

thimble and the coal dropped into the solution. A combination of the two, with the thimble placed inside the alundum cup, was found to be suitable, for even if the thimble did break the amount of coal that would be retained by the cup was not sufficient to materially decrease its porosity. A condenser, as shown in the accompanying figure, was constructed and used in all the extractions. This consisted of a glass tube, which loosely fitted the neck of the Kjeldahl flask, and was supported by the top of it. This tube was drawn to a point with a suitable constriction, from which the extraction cup was suspended by a copper wire basket. This tube was cooled by a test-tube water condenser, which was adjusted to insure complete condensation of the phenol, and yet prevent over-cooling, so the extraction would be at only a few degrees less than the boiling point of the solvent, namely 183°C. The walls of the flask were wrapped with asbestos, although a small opening was left at the level of the extraction cup so that the rate of condensation of the phenol which dropped into the cup could be regulated. The rate of filtration of the solution through the cup was limited, and if the cup overflowed, some of the coal might be carried over into the bottom of the flask. As an additional precaution the coal in the thimble was covered with a tight packing of glass wool. The extraction was stopped when the solution came through colourless. The hot solution was transferred to a 200 cc. distilling flask, and the Kjeldahl washed several times with fresh phenol. This solution was then concentrated to about 30 cc. At all concentrations the solution of the extract in the phenol was a solid at room temperature, so it was necessary to heat it before it could be transferred.

Several methods for the removal of the phenol remaining in the solution were considered. It was evident that there was great danger of also

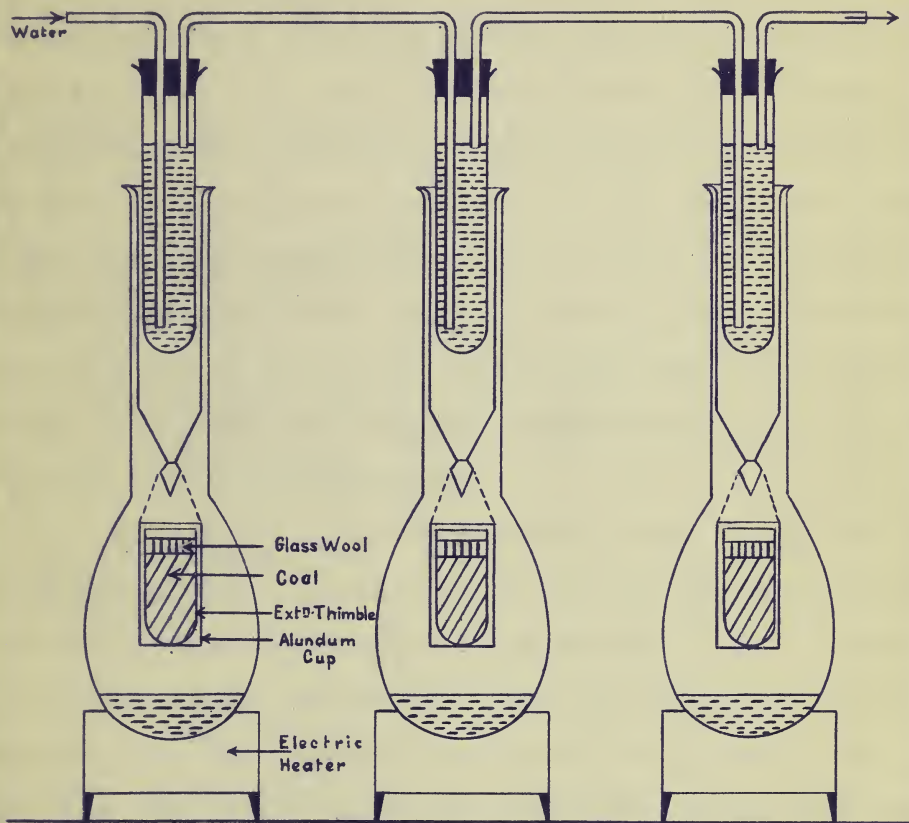


FIGURE - 3

removing any of the phenolic substances that had been dissolved from the coal.

The first method that was tried was based on the work of Frazer and Hoffman¹⁸ who used a weak alkaline solution to wash the extract from the distilling flask, then acidified the whole with hydrochloric acid, and filtered with suction. Frazer and Hoffman were not particularly interested in the quantitative yield but rather in the separation and identification of some of the constituents. On treating the above concentrate with dilute sodium hydroxide, a fraction of the extract seemed to dissolve, for the dark color of the solution spread throughout the entire volume. This was then acidified and a precipitate was thrown down. On filtration, however, the filtrate was still quite dark in colour, which might indicate that some of the extract had remained in solution. This filtration, even with suction was very slow. This method was not investigated further.

Since phenol is volatile with steam, it was thought that it might be possible to remove the last traces of the solvent by steam distillation. Another concentrate was therefore diluted with about 300 cc. of water, and steam distilled until approximately 3 litres of condensate were obtained. The extract was then transferred from the flask to a suitable weighed bottle, dried in an oven at 103°C and weighed. There were several objections to this method. Considerable time was required for each distillation. Also, it was found that some of the extract became attached to the steam delivery tube and the walls of the flask. This was not readily dissolved by any more volatile solvent such as benzene or alcohol, and it was impossible to remove all of it to weigh the extract. Since but 15 grams of coal were used for the extraction, this loss caused a notable error.

Phenol and water are known to be miscible in all proportions at a temperature of 68.4°C. The concentrate was therefore treated with several times its own volume of water. After three or four such extractions, at varying temperatures, no appreciable amount of the solvent had been removed. This miscibility of water and phenol is a property of the two phase system, while in the above we have a three phase system, namely; water, phenol, and extract. The latter is also heterogenous, which might affect the solubility of the phenol in the water.

Parr and Hadley¹⁹ heated the concentrated solution in an oven at 200°C with a stream of ~~natural gas~~ ^{nitrogen} passing through the container to prevent any oxidation, and to help in the removal of the phenol. This was done with one of the above concentrates, substituting natural gas for the nitrogen. The temperature of the oven was gradually increased to 200°C and kept at this maximum for at least two hours after the odour of phenol had entirely disappeared. A definite end point was reached as there was no change in weight during subsequent heating for two hours. This method was employed in all of the extractions made, for it was both effective and simple. It is possible that some of the more volatile constituents of the extract were lost owing to the intense heat. Parr and Hadley, however, found that the weight of the extract plus the weight of the dried residue very nearly equalled the weight of the original coal, so this suspected loss could not be very large.

The standardized method. The method of extraction of coal with phenol was standardized as follows.

Fifteen grams of the air dried coal, ground to pass a 28 mesh sieve, were placed in the extraction thimble and covered with a tight packing of glass wool. This thimble was placed in an alundum extraction cup of medium porosity,

and the whole suspended below the condensing tube by a copper wire basket. Approximately 75 cc. of phenol were placed in the Kjeldahl flask which was wrapped with asbestos, and the above tube with the condenser attached, was inserted (Figure 3). The flask was heated by an electric heater adjusted so that about 20 drops of phenol dropped into the extraction cup every minute. The extractions by this method must occur at only a few degrees below the boiling point of the solvent, 183°C, for the cup was always surrounded by phenol vapour. The extractions were continued until the phenol filtering through the coal and the cup was quite colourless. This took approximately one week, or about 60 hours of extraction as the apparatus was not run at night.

The hot solution was transferred to a 200 cc. distilling flask, and the Kjeldahl washed twice with 10 cc. portions of fresh phenol. The whole was then concentrated to about 30 cc. and poured into a suitable weighed bottle. This bottle was placed in an oven and heated to 200°C with a current of natural gas passing through it. Heat was continued for two hours after all the odour of the phenol had disappeared. The bottle was then removed, stoppered, allowed to cool, and weighed.

Results of phenol extractions. The coals received were extracted with phenol by the method as standardized. The results of these extractions are shown in Table VI.

T A B L E V I.

RESULTS OF PHENOL EXTRACTIONS OF COALS.

Sample	Yields of extracts	
	% original coal	% ash-free dry coal
1. Chinook	14.7	19.0
2. Western Gem	18.2	23.6
3. Costella	10.8	14.3

Table VI - continued.

Sample	Yields of extracts	
	% original coal	% ash-free dry coal
4. Mercoal	18.5	21.5
5. Wall	22.1	27.6
6. Christie	38.3	43.1
7. Beaver	25.0	28.8
8. Mountain Park	32.0	36.9
9. Luscar	28.1	29.8
10. Coleman	36.0	41.9
11. Estevan (Saskatchewan)	9.7	12.6

A sample of the Mountain Park coal, from which 10.9 per cent had been extracted in an autoclave by benzene and alcohol, was treated with phenol and the following result obtained.

Extract amounted to 21.6% of Mountain Park coal residue
equivalent to 19.2% of the original coal.

4. Properties of extracts.

Benzene-alcohol extracts. The extract from every coal was black and amorphous, but a freshly cut surface showed a chocolate-brown colour. At the temperature of the drying oven, 125°C they all appeared to be very viscous liquids, but at room temperature the different samples varied in their hardness. In general, the extracts from the domestic coals were harder than those from the higher grades of coal. The former, and particularly the extract from the Costella coal (Gleichen area), were readily pulverized, yielding a chocolate-

brown powder. The softening point of the extract from the Costella coal was found to lie between 84 and 86°C. This compares favourably with the softening point of commercial montan wax, namely 70.5 to 80.5°C. The extracts from the bituminous coals were, however, distinctly softer. At room temperature, they could be cut and moulded, yet would crumble if struck.

The deep colour of the solution when the extract was dissolved in the original solvent, prevented the determination of the acid and saponification values, which would have more definitely ^{*proved or disproved the*} identity ~~of~~ the extract as montan wax. Unsuccessful attempts were made to remove this colour by treating the solution with bauxite, in the hope that the aluminum hydrate would form a lake with the colouring matter. The method, as described in the British Patent literature²⁵, of bleaching the extract by treatment with chromic acid in the presence of acetic acid was also unsuccessful. The late receipt of the details of this method prevented further experiments with it.

Rogers²⁶ states that montan wax is bleached by steam distillation with superheated steam. The extract from the Mountain Park coal was used for the following experiment because the yield was sufficient to make it possible that commercial development might follow if the extract could be identified as montan wax. Steam was preheated by passing it through a copper coil surrounding the test tube containing the extract, the whole being immersed in an oil bath, and led to the bottom of this test tube. A suitable water condenser was also attached. By this method the temperature could be raised to 200°C. As this did not appear to be high enough, the oil bath was replaced by an iron pipe, open at both ends, about two feet in length and three inches in diameter. Heat was supplied by a Bunsen burner placed at the bottom. In this way temperature of from 400 to 450°C was thought to be attained before the test tube was destroyed. The first fraction that was steam distilled was

a yellow liquid of pleasant odour. This probably consisted of the liquid hydrocarbons, and fatty acids, as superheated steam may saponify the resins and waxes present. The second fraction was a yellow wax, very soft at room temperature. As the heat was increased, the distilled wax became darker in colour and much harder. The final residue was a chocolate-brown, glossy, very hard substance. Hence it appeared that steam distillation had resulted in a fractionation of the extract, and probably the saponification of some of the resins and waxes. Hence this method did not bleach the wax as suggested by Rogers. The extract probably did not consist of montan wax, as Mountain Park coal is of the bituminous grade, and the waxes and resins have been partly changed to the hydrocarbons, as suggested by Wheeler and others.

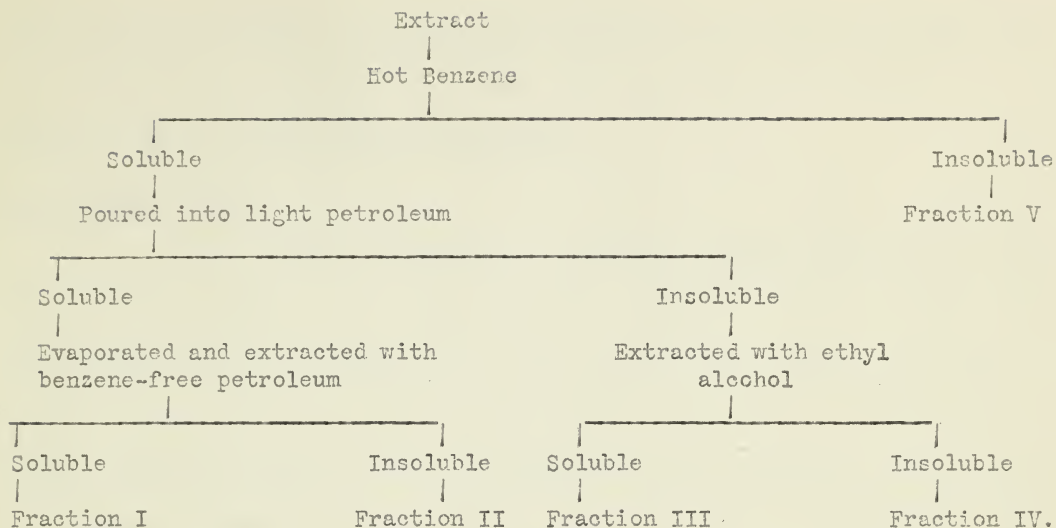
It was thought that at least a partial fractionation of the extract obtained from the various coals might indicate some difference between them. The method employed was that used by Bone and others, and described previously.

Although the extract was entirely soluble in the original solvent, a mixture of benzene and methylated spirits, it was found to be but partially soluble in benzene. The sample was well macerated and treated with hot benzene, the extractions being continued until the solvent was quite colourless. The residue, a black powder, somewhat harder than the original extract, was treated with methylated spirits, as its removal from the coal was thought to be due to the presence of this solvent. However, it was not entirely soluble in the methylated spirits. From this two conclusions were possible, either some chemical action such as one of oxidation, had occurred after the extraction and altered the extract, or the mixture of solvents was more efficient than the two solvents used consecutively would have been. The first was not con-

sidered probable for the extract was entirely soluble in the original solvent, and the danger of oxidation should not be great unless the extract was heated in the air. The second is quite possible for benzene having a dielectric constant of 2.28 at 18°C may be termed a non-polar solvent, while methylated spirits, being a mixture of ethyl and methyl alcohol with dielectric constants of 25.8 and 33.7 at 18°C respectively, is more polar. Hence a mixture of these solvents can remove both polar and non-polar stresses on the molecule and render it soluble. The substances insoluble in either benzene or methylated spirits, but soluble in the mixture, require both a polar and a non-polar solvent to render them soluble. Illustrations of similar phenomena are not uncommon. Prolamines will dissolve in 60 per cent alcohol, yet they are practically insoluble in either water or absolute alcohol.

The benzene solution prepared from the extract as above was concentrated and poured into light petroleum from which a brown flocculent precipitate settled out. The whole was allowed to stand for 24 hours, as this seemed necessary for complete precipitation. It was filtered; the precipitate then treated with ethyl alcohol to separate it into a soluble and an insoluble fraction; the filtrate evaporated to dryness and treated with benzene-free petroleum. The product was again filtered and the filtrate evaporated. The scheme is shown in the following chart.

The fractions are numbered similarly to the method adopted by Bone. The fractionation was completed on two extracts, namely from Mountain Park and Western Gem (Drumheller area) coals.



Fraction I in both samples was a dark red-brown, resinous material, fairly soft at room temperature. The only difference noted was that the one from the domestic coal was slightly the harder.

Fraction II in the extract from the bituminous coal was a red-brown powder, while in that from the domestic coal was a dull yellow powder.

Fraction III was a brown, brittle powder in both extracts, slightly darker in colour in that from the bituminous coal.

Fraction IV in both cases was a brown powder. The particles from the extract of the domestic coal were the harder.

Fraction V was in both cases a black powder similar to the original extract. It was partially soluble in alcohol, but no difference was apparent between the fractions thus obtained.

The fractions isolated from the extract of the domestic coal, were in general, harder than those from the bituminous extracts. This might be expected from Wheeler's conclusions already stated, that the waxes and resins of the lignites are changed to the hydrocarbons of the bituminous coals as the coal is matured. The fractions, on the whole, compared favourably with those separated and described by Bone. Since the amount of the extracts available for these fractionations was small, particularly in the case of

the Western Gem sample, and there was considerable loss in filtration, the percentage error was thought to be too large to attach any value to the amount of each of the fractions obtained.

Ultimate analyses.

It was thought interesting to ascertain whether the extracts from the different types of coal were essentially alike, or whether extracts from high oxygen coals, for example, had also a high oxygen content. In other words, it was desired to trace the variation in the carbon, hydrogen, and oxygen content of the extracts, in comparison to the ultimate composition of the different grades of coal. Three samples were selected to represent the three types of coal extracted, namely the domestic or lignite, the sub-bituminous, and the bituminous. These were respectively Costella, Mercoal, and Mountain Park coals.

Ultimate analyses typical of the coals from these areas were obtained from the Industrial Research Laboratories of the University, and are given on the pure coal, dry basis. As no analysis had been made of the coal from the Gleichen area, the probable analysis of the Costella coal was calculated by interpolation between the coals of the Drumheller and Champion areas, reasoned on the basis of the average moisture content. These ultimate analyses are shown in Table VII.

T A B L E V I I .

ULTIMATE ANALYSES OF THREE ALBERTA COALS (on pure coal dry basis)

Coal	Carbon %	Hydrogen %	Oxygen %
Costella	76.9	5.2	18.0
Mercoal	79.6	5.1	15.3
Mountain Park	87.5	5.5	7.0

The benzene-alcohol extracts from these three coals were analysed with the results shown in Table VIII.

T A B L E V I I I .

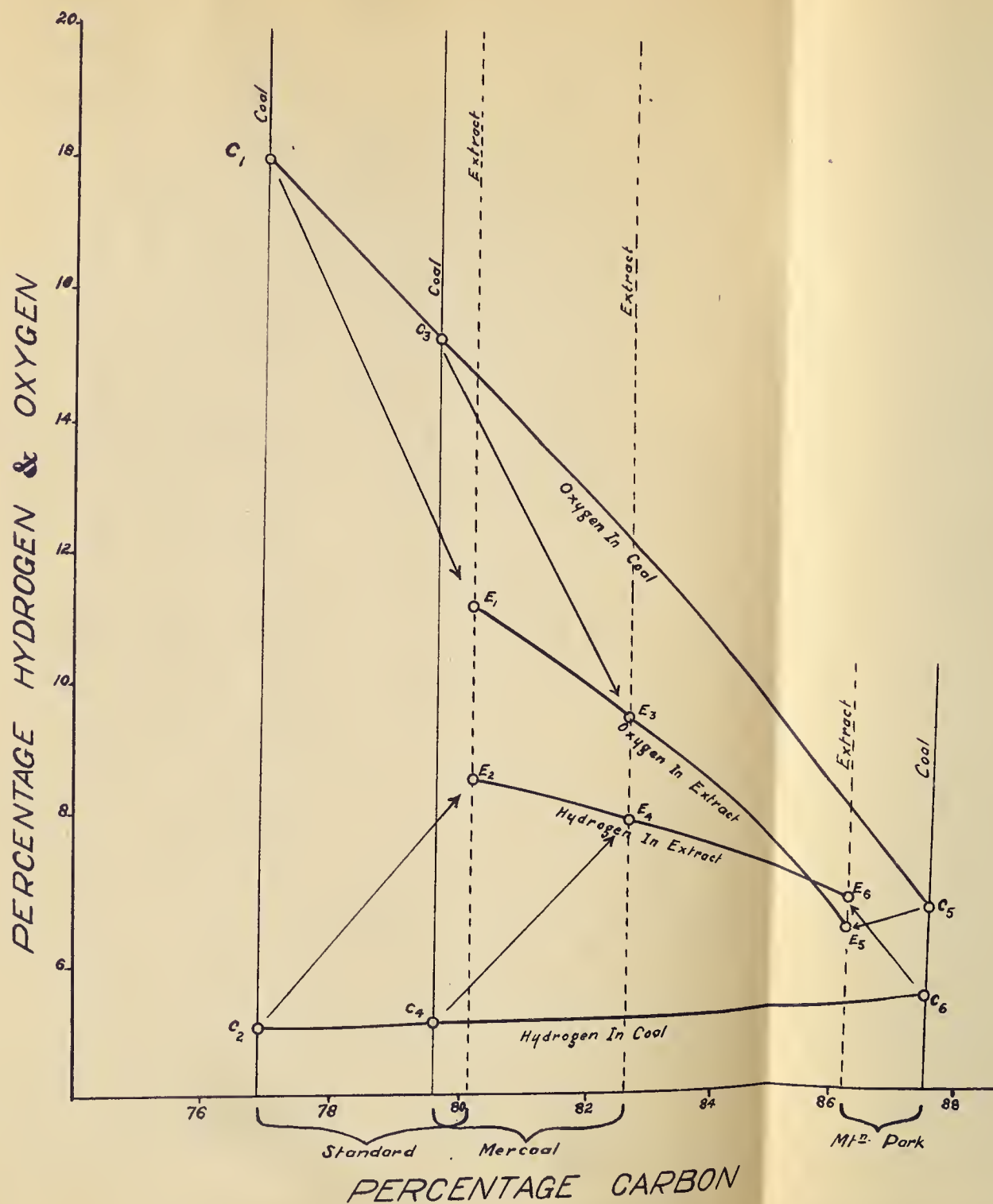
ULTIMATE ANALYSES OF EXTRACTS OF THREE ALBERTA COALS

Coal	Carbon %	Hydrogen %	Oxygen %
Costella	80.20	8.60	11.20
Mercoal	82.45	7.95	9.60
Mountain Park	86.20	7.05	6.75

The results given in Tables VII and VIII are shown in the accompanying graph, the percentages of hydrogen and oxygen being plotted against the percentage of carbon. The points C₁, C₃, and C₅, show the oxygen contents of the three coals; E₁, E₃, and E₅, the oxygen contents of the three extracts; C₂, C₄, and C₆, the hydrogen contents of the three coals; and E₂, E₄, and E₆, the hydrogen contents of the three extracts.

It is evident that in the lignite and sub-bituminous samples the carbon content of the extracts is greater than that of the coals. The reverse is true, however, in the case of the bituminous sample. The oxygen content of the extract is less than that of the coal in every case, while the hydrogen content of the extract is always greater than that of the coal. Again, although the variation in the oxygen contents of the coal is large, namely from 18.0 per cent to 7.0 per cent, in the extracts the variation is only from 11.20 per cent to 6.75 per cent. This is shown by the line joining C₁, C₃, and C₅, and the line through E₁, E₃, and E₅. The variation in the hydrogen contents of the three coals, and the three extracts, does not show the same characteristic. This might be explained by the small change in the hydrogen content as a coal matures from the lignite to the bituminous grade.

SHOWING RELATION OF ULTIMATE COMPOSITION OF COALS & EXTRACTS



The most characteristic difference between coals of different ranks is the higher ulmin content of the less mature coals. As these ulmins have a high oxygen and hydrogen content and as they do not figure in the extract, it is natural that chemical differences between extracts are not as great as those in the coals. Also the rate of loss of oxygen in coals and extracts is greater than that for hydrogen, which would be expected, as the soluble waxes and resins present in lignites and brown coals are thought to have been changed to some extent to the soluble hydrocarbons of the bituminous coals, a change which involves chiefly a loss of oxygen.

Properties of phenol extracts.

There were not the same apparent differences between the phenol extracts from the various coals tested, as between the corresponding benzene-alcohol extracts. The phenol extracts were black, brittle substances, readily pulverized. Their softening points were not determined but they were undoubtedly much higher than those of the benzene-alcohol extracts. At 200°C, the temperature at which they were dried, the extracts appeared to be very viscous liquids. Their solubility in other organic solvents, such as ether, chloroform, acetone, alcohol, and benzene, was quite low, although it was sufficient to give the solvent an appreciable colour.

A complete fractionation scheme, with the ultimate analyses of the fractions obtained, is described by Frazer and Hoffman¹⁵, but it was not considered necessary to treat the extracts similarly. It was noted, however, that the extract was appreciably soluble in 10 per cent alcoholic potassium hydroxide. Hence a sample of the Mountain Park extract was treated with this reagent, and the solution kept warm for 24 hours. The insoluble portion, which was about 25 per cent of the total, was a black, brittle powder, apparent-

ly much the same as the original extract. The filtrate was neutralized with hydrochloric acid, whereby a heavy flocculent precipitate was thrown out of solution. This was filtered through a #42 Whatman filter paper without suction, for the precipitate being a resinous one, soon filled the pores of the paper when suction was applied. The filtration was very slow, and if large amounts had to be treated, some means of preventing oxidation might have to be adopted. An attempt was made to dry this precipitate in the oven at 75°C, but it began to turn white as though beginning to ash. This change was not examined further. The filtrate was heated to remove the alcohol, and a hard, brown, resinous material was thrown out of solution.

Treatment of the extract with alcoholic potassium hydroxide probably resulted in the saponification of the esters or waxes present. The potassium salts of the acids thus formed, as well as of any acids present as such in the extract, are soluble in the alcohol. On the addition of hydrochloric acid, some of these acids may be thrown out of solution which would account for the flocculent precipitate. The hard, resinous portion recovered later, probably consists of fatty acids, soluble in alcohol. No further attempts were made to identify any of the components of this extract.

The extraction of the residue of the Mountain Park coal, after extraction with benzene and alcohol, yielded 21.6 per cent of this residue, which is equivalent to 19.2 per cent of the original coal, since 10.9 per cent of the coal had been removed by the benzene-alcohol extraction. The total 30.1 per cent is of the same order as the 32.0 per cent extract obtained on the extraction of the original coal with phenol. This suggests that the phenol removed from the coal all that portion soluble in benzene and alcohol, as well as some other fraction.

CHAPTER V.

DISCUSSION OF RESULTS.

Many attempts have been made by investigators to correlate the solubility of the coal with some other determination or property. As yet the only success has been in noting that from bituminous coals, the yield, in general, varies directly with the volatile matter content of the coal. Low volatile British coals have been cited as giving as low as 7 per cent extract, while high volatile British coals gave, under the same conditions, 12 per cent or even higher. No definite conclusions can be drawn from the small number of Alberta bituminous coals tested. Several exceptional results were obtained, chiefly from the Luscar and the Coleman samples, both of which showed very low yields on extraction.

No indication of the amount of extract which might be expected from a brown coal or lignite is yet apparent. In Germany, only those coals which yield over 10 per cent extract are worked for their montan wax content, and wide variations are found in any field. Bone obtained yields of 15 per cent from the Morwell coal of Australia, only 5 per cent from the Saskatchewan coals, and 2 to 5 per cent from Alberta lignites. Wood and Nicholas were able to extract 12 per cent of the Nigerian lignite with benzene. The yields obtained from the lignite coals of Alberta in this investigation, varied from about 2 to 5 per cent, which are of the same order as those obtained by Bone. It is fairly evident that the amount of extract from an immature coal is dependent on the original vegetable matter, and on the transformations of this vegetable matter previous to becoming covered with an impervious layer.

In order to obtain some idea of the comparative yields of extracts from the various coals extracted, and the relation those yields might have to any other determination or property of the coal, Table 9 was drawn up.

TABLE IX.

ANALYSES AND SOLUBILITIES OF COALS TESTED

Coal	Moisture		Volatile Matter		Fixed Carbon		Fuel		Dowling's		Benzene-Alcohol		Phenol Extract	
	%	(a)	(b)	%	(a)	(b)	Ratio	Ratio	Extract	Ratio	Extract	%	(a)	(b)
Chinook	16.8	34.5	44.9	42.2	55.0	55.0	1.2	1.7	1.9	2.4	14.7	19.0	14.7	19.0
Western Gem	14.8	32.0	41.9	44.3	58.1	58.1	1.4	1.9	3.8	5.0	18.2	23.6	18.2	23.6
Costella	14.0	32.5	43.0	43.1	57.0	57.0	1.3	1.9	3.1	4.1	10.8	14.3	10.8	14.3
Mercoal	5.4	37.4	43.5	48.6	56.5	56.5	1.3	2.8	4.9	5.7	18.5	21.5	18.5	21.5
Wall	7.5	34.9	43.7	45.0	56.3	56.3	1.3	2.9	8.5	10.6	22.1	27.6	22.1	27.6
Christie	1.7	31.8	35.8	57.1	64.2	64.2	1.8	4.1	2.2	2.5	38.3	43.1	38.3	43.1
Beaver	0.9	30.9	35.5	56.0	64.4	64.4	1.8	4.4	8.5	9.6	25.0	28.8	25.0	28.8
Mountain Park	1.0	30.8	34.8	57.6	65.2	65.2	1.9	4.5	10.9	12.5	32.0	36.2	32.0	36.2
Luscar	0.6	27.1	28.7	67.2	71.2	71.2	2.4	5.7	.3	.3	28.1	29.8	28.1	29.8
Coleman	0.6	25.4	29.6	60.5	70.5	70.5	2.4	5.5	1.6	1.9	36.0	41.9	36.0	41.9
Estevan	16.6	33.9	44.3	42.7	55.8	55.8	1.2	1.8	2.7	3.5	9.7	12.6	9.7	12.6

(a) on basis of original coal. (b) on basis of ash-free dry coal.

Dowling's Ratio Fixed Carbon + $\frac{1}{2}$ Volatile Matter
 Moisture + $\frac{1}{2}$ Volatile Matter

Where Fixed Carbon, Volatile Matter and Moisture are on basis of air-dried coal.

From this table it is apparent that, in general, the yield of extract obtained by the benzene-alcohol extraction increases with the maturity or grade of the coal up to a maximum, and then suddenly decreases. This is probably best exemplified by a comparison of the yields obtained and the so-called "Dowling's Split Ratio". The greatest yield obtained was that from Mountain Park coal, with a ratio of 4.5, and a fixed carbon content of 65.2 per cent on the original coal basis. The yield from the Coleman coal which has a ratio of 5.5 and a fixed carbon content of 70.5, was much less, namely 1.6 per cent, and from the Luscar sample the yield was even smaller. The outstanding exception to this general rule is the coal from the Christie mine with a yield much below that which might be expected.

The same general statement as to the yields obtained might be made in regard to the phenol extraction of the coals. There is not, however, the sudden decrease in yield for coals of a higher grade than the Mountain Park. In fact the yield obtained from the Coleman sample was even larger. Again, the coal from the Christie mine is an exception, but in this case the yield was larger rather than smaller than expected.

The high yields of extracts obtained from bituminous coals conforms with the conclusions of Wheeler, Bone, and others. The extract from this grade of coal contains, besides hydrocarbons, waxes, and resins, substances formed due to the transformation of the protein and cellulosic constituents of the vegetable matter. These were called "cellulosic bodies" by Wheeler, and constitute the alpha and beta fractions obtained by treating the pyridine extract of the coal with chloroform. Bone has termed them "humic bodies", and separated them from the benzene extract by treatment with light petroleum and ethyl alcohol. As the coal still further matures, however,

these substances as well as, in all probability, the waxes and resins, are broken down. This would account for the lower yield of extract obtained from the higher grades of coal.

This gradual increase in the benzene-soluble fraction, as the coal matures up to the rank of the bituminous coal, suggests that the hydrocarbon and wax content might remain fairly constant, due to its resistance to bacteria action and oxidation. The increase would then be due to the formation of cellulosic bodies, a point which could be confirmed by a quantitative separation of the extracts obtained, to determine the actual hydrocarbon and wax content, that is, Wheeler's gamma fraction. The results might indicate the similarity, at least with respect to the fatty oil and wax content, of the vegetable matter deposits from which the coals were formed. Before this further investigation is undertaken, the writer is of the opinion that the extraction with pyridine should be tried, and the general application of Wheeler's methods should be examined more closely than was possible in this work on Alberta coals.

CHAPTER VI.

SUMMARY AND CONCLUSIONS.

1. A Soxhlet method was devised for the extraction of about one kilogram of coal with organic solvents at atmospheric pressure.
2. Samples of coal from the Edmonton area were extracted with benzene and xylene at atmospheric pressure. The yields of extract were less than 0.4 per cent of the air-dried coal.
3. A sample of lignite from Morwell, Australia, was extracted with benzene under the same conditions. The yield was seven or eight times as great as that from the coal of the Edmonton area, but was still low.
4. The coal from the Edmonton area was extracted using the same methods and solvents, but in a reducing medium obtained by bubbling sulphur dioxide through the solution. The yield of extract was not increased.
5. A Soxhlet method was devised for the extraction of about 700 grams of coal with solvents at high pressures, and the above coals extracted with benzene. The yields were about four times as large as before, namely, 4 to 5 per cent from the Morwell coal, and 1.5 to 2 per cent from the Edmonton coal.
6. The Edmonton coal was extracted under pressure, with a mixture of 75 per cent benzene and 25 per cent methylated spirits. The yield was still further increased.
7. Ten selected Alberta coals, and a sample of coal from Estevan, Saskatchewan, were extratted with this mixture of benzene and alcohol.
8. A sample of Edmonton coal was preheated in an atmosphere of hydrogen, and another in an atmosphere of oxygen, but the yield of extract on subsequent extraction with benzene and alcohol was not increased in either case.

9. A Soxhlet method was devised for the extraction of coal with phenol at approximately the boiling point of the solvent.

10. Various methods were investigated for the removal of the last traces of phenol from the extract.

11. The ten selected coals were extracted with phenol.

12. The properties of the extracts were studied.

13. The benzene-alcohol extracts were fractionated by the method devised by Bone, for the segregation of the hydrocarbons, the waxes, and the humic substances.

14. The ultimate analysis was determined of a benzene-alcohol extract from each of the three grades of coal tested, and the results compared with the ultimate analyses of the same coals.

Conclusions.

The solubility of the Alberta coals examined in the solvents benzene, xylene, and mixtures of these with alcohol, is not appreciable unless the extractions are made at pressures somewhat higher than atmospheric pressure. With any solvent the amount of the coal dissolved varies largely with the coal used. The extract obtained from some lignites resembles the crude montan wax as described in the literature, at least in so far as its high softening point is concerned, but the yield is not large enough to warrant consideration of an attempt to establish a montan wax industry. Treatment of the heated coal, previous to extraction, with hydrogen or oxygen does not increase the yield of extract. It is still possible, although hardly probable, that other lignitic coals of Alberta will give larger yields.

The yields of extracts obtained from some of the bituminous coals examined is considerably larger than those from the lower grades of coal.

Their low softening points indicate, however, that they are not montan wax. The extracts resembled those obtained by Bone from British bituminous coals. Also the fractions of the extract from the Mountain Park coal are similar to those isolated in the same way from the British bituminous coals by Bone, who at no time considers the extracts from such coals, montan wax. The waxes and resins of the lignitic and immature coals have probably been changed to the hydrocarbons of the bituminous coals, as suggested by Wheeler, Bone, and others. This would involve a larger reduction in the oxygen than in the hydrogen content of the extract. Comparison of the ultimate analyses of the extracts and of the coals shows this larger decrease in oxygen content. The hydrocarbon and wax content is one of the determinations made in the "Rational Analysis of Coal" suggested by Wheeler.

Phenol was found to be a much more efficient solvent than those mentioned above. It is unfortunate that the types of compounds present in the extracts so obtained have not been identified to the same extent.

The yields of benzene-alcohol extracts from Alberta coals increased in general with the maturity of the coal up to a certain stage, but they were notably lower with the further matured coals. The yields of phenol extracts from the same coals were, on the whole, higher with the more mature coals, and even high with the most mature coals. Comparison of the yields from the benzene-alcohol extractions, and from the phenol extractions, showed, in places, some remarkable disconformities.

CHAPTER VII.

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